BASE-EXCHANGE EQUILIBRIA IN SOILS AND OTHER EXCHANGE MATERIALS

BY

SIGURD WALTER MELSTED

B. S., North Dakota Agricultural College, 1938

M. S., Rutgers University, 1940

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN AGRONOMY IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS, 1943

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I. INTRODUCTION

In recent years the use of exchange materials in research and industry has continually increased. Their use to remove either cations or anions from solution, particularly for water softening or solution purification, is an accepted procedure. But the importance of base-exchange phenomena is not limited to research or industrial procedures. Soil chemists have long known that many of the chemical and physical properties of the soil are directly related to their exchange properties. Thus the prevention of the loss of plant nutrients by leaching is controlled by the exchange properties of the soil colloid. The so-called available plant nutrients, especially the cations, are those held on the exchange surface of the soil colloid and released to the root surface or soil solution through exchange phenomena. Although the importance of exchange reactions has been recognized for a long time, the dynamics of the ion-exchange phenomena are little understood.

Bray has published a series of "f" values for the various ions found in soils when associated with a soil colloid. These so-called "f" values correspond to what Jenny refers to as the "oscillation volume" of the various ions. It was the purpose of this investigation to check these "f" values as well as to determine some of the factors (and their relative magnitude) that exert an influence on the exchange equilibria. Two types of exchange equilibria were investigated, namely (1) the "static" equilibria and (2) the leaching equilibria.

II. PROCEDURE

Two types of equilibria were used. The "static" type, where a definite amount of exchange material is shaken with a definite amount of salt in a definite volume, and the "leaching" type, where a definite amount of exchange material is exhaustively leached with a solution of a definite ion composition and concentration. Various exchange materials were used, including natural soils, natural silicate minerals, and

synthetic exchange materials. The ion distribution on the exchange material was determined by leaching the materials, after equilibrium, with NH_4Ac and determining the individual ions according to the usual base-exchange procedure.

III. RESULTS AND CONCLUSIONS

The published "f" values of Bray were found to be applicable for natural surface soils, while the determined "f" values for the pure silicate minerals and organic free "B" horizon materials were slightly lower. For the "static" type of equilibria, where the amount of any one ion in solution is not sufficient to dominate the exchange surface, the following simple mass action relationship was found to exist.

$$A_1 = \frac{A.f_a}{A.f_a + B.f_b + C.f_c + \ldots + N.f_n} \text{ x m.e. anion}$$

where A_1 = m.e. of A in solution after equilibrium

A,B,C . . . .N = total m.e. of each ion in the system

$f_a, f_b, f_c \ldots . f_n$ = the "f" values for the respective ions

A study of the effect of the concentration of the leaching solution on the final distribution of the ions on the exchange surface definitely showed that as the leaching solution of mixed ions is concentrated the monovalent ions will increase while the divalent ions will decrease on the exchange surface. A study of the effect of the ratio of the ions in a leaching solution, at constant concentration, on the final distribution of the ions on the exchange surface showed that as the ratio between two ions in solution widened their relative ratio on the exchange surface narrowed. This relationship between the ratio and the concentration of the ions in the leaching solution and their final distribution on the exchange surface, for a natural soil material and the ions Ca and K, may be expressed mathematically as follows, $y - 27 \log x = 80 - 31 \log r$ where y is the percent K on the exchange surface, x is the total normality of the leaching solution, and r is the Ca/K ratio in the leaching solution.

The change in the percent K on the exchange surface with changes in the concentration of the leading solution is amply demonstrated with a natural soil material and 1:1 Ca:K chloride leaching solutions. When leached with an 0.05 N solution the exchange surface contained 47 percent K and 53 percent Ca, but when leached with a 1.0 N leaching solution the exchange surface contained 77 percent K and 23 percent Ca.

The effect of the total concentration of a leaching solution of ions of the same valence on their distribution on an exchange material will depend on the nature of the exchange material. For the monovalent ions K and Na the percent Na on all exchange materials studied decreased with increasing concentration, when these ions were present in a 1:1 ratio in the leaching solution. For the divalent cations Ca and Mg the percent Ca on the exchange surface increases with concentration on soils and natural silicate minerals but decreases with increasing concentration on Zeo-Karb and Amberlite, when these materials are leached with a leaching solution containing these ions in a 1:1 ratio. Concentration seems to have very little effect on the percent H adsorbed by an exchange surface. In general H adsorption tends to decrease with increasing concentration when in competition with any cation in a 1:1 ratio and in solutions of 0.05 N or greater.

The exchange material used is an important factor in determining the distribution of the cations on the exchange surface. Soils and the natural silicate minerals behave as a group but they differ from the synthetic exchange materials. As an example of the effect of the exchange material, when Permutit and Amberlite were leached by a 1.0 N leaching solution of 1:1 Ca:K chloride the Permutit exchange surface contained 8 percent Ca and 92 percent K while the Amberlite exchange surface contined 77 percent Ca and 23 percent K. It is this natural tendency of Amberlite to adsorb Ca that makes it superior to Permutit, which preferentially adsorbs K, as a water softener. The success of an exchange material for the purification of a solution or for the concentration of ions may depend as much on the character of the exchange material as on its stability or exchange capacity.

All the natural soils and natural silicate minerals studied preferentially adsorb K from a concentrated leaching solution containing equal normalities of Ca and K. This suggests that when K fertilizers are applied to a soil in a concentrated form the probable leaching losses are not in proportion to the increase in the concentration of the fertilizer added.

VITA

The author was born November 23, 1911 at Gardar, North Dakota. He received his early education in the rural schools of Gardar, North Dakota. The last two years of his high school education were taken at the Walsh County Agricultural Training School at Park River, North Dakota, and he graduated from there in May 1930. The following four years were spent in miscellaneous farming activities.

He entered the North Dakota Agricultural College in September, 1934 and was graduated in June, 1938 with a B.S. degree in Agriculture. He enrolled in the Graduate School of Rutgers University in September, 1938 with a research assistantship in soil testing and he received his Master of Science degree June, 1940. In September, 1940 he entered the Graduate School of the University of Illinois. He was employed as a half-time assistant in Soil Survey Analysis from September 1940 to April 1942 when he became a full-time assistant in Soil Survey Analysis.

The author is an active member of Sigma Xi, Phi Kappa Phi, Gamma Sigma Delta, and Alpha Zeta.

PUBLICATIONS

Melsted, S. W. A chemical study of quick-test technics for potassium and calcium. Jour. Am. Soc. Agron. 34:533-43, 1942.

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